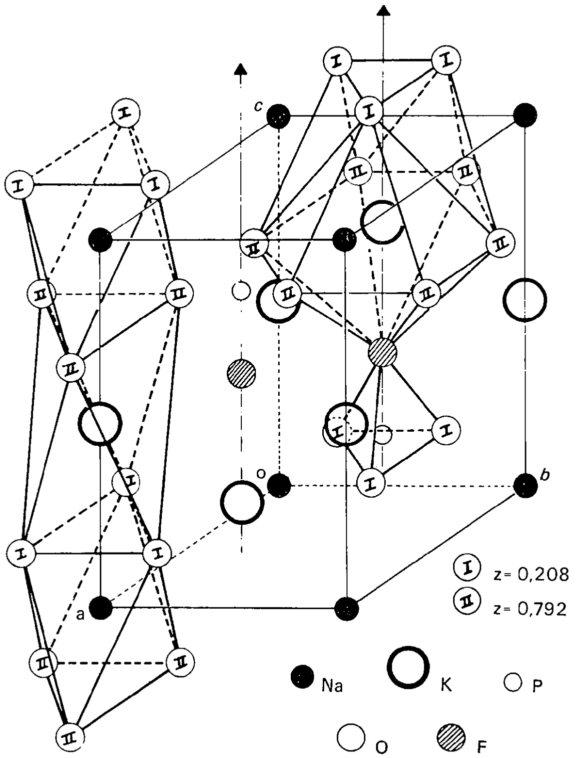

Fig. 2. Environnement des cations dans la structure $NaK_3(PO_3F)_2$.

Sur l'axe ternaire, on a un empilement constitué de polyèdres centrés sur l'atome de potassium et de tétraèdres PO_3F. L'atome de fluor est commun à ces deux polyèdres (Fig. 2).

Cette structure est donc caractérisée par un empilement d'anions parallèlement à l'axe *c*. On observe:

– en $(\frac{1}{3},\frac{2}{3})$ puis $(\frac{2}{3},\frac{1}{3})$ une succession d'environnements alternativement tétraèdrique (PO_3F) puis polyédrique autour de K [site (*d*)] présentant une face puis un sommet commun (F).

– en (0,0) une succession de groupements octaèdriques déformés présentant une face commune: celle perpendiculaire à l'axe *c*.

Ces ensembles mettent en commun des atomes d'oxygène qui assurent la rigidité de l'édifice.

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The Conformation of Non-Aromatic Ring Compounds. XC. The Crystal Structure of the 3,5-Dinitrobenzoate Ester of Pyrocalciferol at −170°C

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Crystals of the 3,5-dinitrobenzoate ester of pyrocalciferol are monoclinic. The lattice constants at −170°C are $a=11{\cdot}28$ (1), $b=11{\cdot}27$ (1), $c=12{\cdot}537$ (5) Å and $\beta=93{\cdot}25$ (5)°. The space group is $P2_1$ and $Z=2$. The structure was solved by Patterson-search methods and refined by the least-squares technique, using graphite-monochromatized Mo $K\alpha$ diffractometer data. Despite the unusual $9\alpha,10\alpha$ configuration the molecule is not severely strained: chairs *A* and *C* display some deformation near their junctures with rings *B* and *C*, ring *B* has the expected 1,3-diplanar form and ring *D* has a conformation intermediate between a $C_s(13\alpha)$ envelope and a $C_2(16)$ half-chair form ($\Delta=15{\cdot}5$, $\varphi_m=47{\cdot}5°$).

Introduction

This paper is a continuation of earlier reports on structural studies in the vitamin D series [*cf.* vitamin D: Knobler, Romers, Braun & Hornstra (1972); ergosterol: Braun, Hornstra, Knobler, Rutten & Romers (1973); lumisterol: de Kok & Romers (1974)]. The 3,5-dinitrobenzoate ester of pyrocalciferol is obtained by heating the corresponding previtamin D ester. The structure of the corresponding isopyrocalciferol ester, a by-product of the same reaction, will be discussed in a forthcoming paper (de Kok, Hogendorp & Romers, to be published).

The scheme of photochemical and thermal conversions of numbers of the vitamin D family was discussed by Sanders, Pot & Havinga (1969). According to the IUPAC–IUB (1969) rules the systematic name of the title compound (hereafter PCD) is 10α-ergosta-5,7,22-trien-3β-ol 3′,5′-dinitrobenzoate. The chemical formula and the numbering of the atoms are indicated in Fig. 1(*a*) and (*d*).

Experimental

The heating product of the previtamin D ester was purified by fractional crystallization from solutions in acetone. Orange lath-shaped monoclinic crystals of PCD were obtained by recrystallization from light petroleum. The lattice dimensions at 20 and −170°C were measured manually on a three-circle diffractometer using Cu $K\alpha(\lambda=1\cdot5418$ Å) and Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å) (see Table 1). The reflexions $0k0$ are absent for k odd. Since PCD is optically active the space group is $P2_1$.

Table 1. *Crystal data for PCD* (3,5-*dinitrobenzoate ester of pyrocalciferol*)

Molecular composition $C_{35}H_{46}O_6N_2$, $M=590\cdot7$
Two molecules per unit cell, space group $P2_1$

20°	−170°
$a=11\cdot21$ (1) Å	$a=11\cdot285$ (5) Å
$b=11\cdot14$ (1)	$b=11\cdot27$ (1)
$c=12\cdot83$ (1)	$c=12\cdot537$ (5)
$\beta=93\cdot8$ (1)°	$\beta=93\cdot25$ (5)°
$d_{obs}=1\cdot20$ g cm^{-3}	$F(000)=736$
$d_{calc}=1\cdot21$ g cm^{-3}	μ(Mo $K\alpha$)$=0\cdot85$ cm^{-1}

Observed significant reflexions: 3302
Reflexions less than twice the background: 562
Non-observed reflexions within $\theta=29°$: 580

The reflexion intensities of a crystal with dimensions 0·5 × 0·3 × 0·2 mm were collected at −170°C with a three-circle diffractometer using Mo $K\alpha$ radiation. The θ–2θ scanning mode with scan width varying between 0·8 and 1·4° was employed and the radiation was monochromatized with graphite.

One of the standard reflexions $1\bar{2}2$, $2\bar{1}2$ and $\overline{21}1$ was measured after each series of 19 reflexions. The standards were used for the calculation of a polynomial function of the exposure time in order to correct for loss of scattering during the exposure. The maximum glancing angle was 29°. Since the linear absorption coefficient for Mo $K\alpha$ radiation (Table 1) is very small no absorption correction was applied. The intensities were reduced to structure factors in the usual way. An overall isotropic B value (1·49 Å^2) was obtained from a Wilson plot.

Solution of the structure

Attempts to solve the structure by direct methods were unsuccessful. The solution was achieved by means of the Patterson search method of Braun, Hornstra & Leenhouts (1969). We introduced as a known part of the structure seven carbon atoms, C(31)···C(37), two nitrogen atoms, N(1) and N(2), and four oxygen atoms, O(1), O(4), O(5) and O(6) belonging to the 3,5-dinitrobenzoate group, hereafter DNB see (Fig. 1). This part was supposed to be planar, with bond angles of 120°, aromatic C–C distances of 1·39 Å, C–N distances of 1·44 Å, N–O distances equal to 1·16 Å and having an external C–C bond with a length of 1·48 Å. The orientation and position of this moiety in the unit cell with the lowest MOF value (measure of fit with the Patterson function) proved to be the correct solution.

The remaining unknown atoms were added one by one to the known group in such a way that each time the atom with the lowest MOF value for the proposed position was chosen from the list of candidates. In this way all but one of the heavy atoms were correctly located. The correct position of the wrongly located atom [*i.e.* C(26) erroneously bonded to the carbonyl oxygen atom O(2)] was, however, present with a higher MOF value in the list of proposed sites. The required computer time was 25 min on an IBM 360/65 computer.

Refinement

The least-squares refinement of positional and thermal parameters was performed in the usual way, taking scattering factors for carbon, nitrogen and oxygen from *International Tables for X-ray Crystallography* (1962) and for hydrogen from Stewart, Davidson & Simpson (1965). The initial model resulted in an R value of 26·4 % $[R=\sum(||F_o|-|F_c||)/\sum|F_o|$, $R_w=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}]$. After refinement with individual isotropic B parameters R dropped to 11·3 %.

The molecule contains 46 hydrogen atoms, 36 of which were found in a difference Fourier map; the remaining hydrogen atoms were introduced at calculated positions. The refinement was resumed with isotropic B parameters for the light atoms (4 × 4 blocks) and with anisotropic thermal U_{ij} parameters (9 × 9 blocks). The anisotropic temperature factor is defined as $\exp[-2\pi^2\sum_{i,j}h_ih_ja_i^*a_j^*U_{ij}]$, $i,j=1,2,3$. The individual reflexions were weighted according to the formula $w(hkl)=1/\sigma^2(hkl)$. The variance $\sigma^2(hkl)$ was calculated from $\sigma^2(hkl)=\sigma^2$ [counting statistics $+0\cdot03$ $F^2(hkl)$]. Up to the final stages of the refinement only significant reflexions were included in the calculations. During the final two cycles, non-significant reflexions (Table 1) were also included in the data set. Including non-significant reflexions the final R and R_w values are 6·39 and 5·00 %;[*] without non-significant reflexions these values are 5·37 and 4·86 %. The positional and thermal parameters of the heavy atoms are listed in Tables 2 and 3. The positional coordinates and B values of the hydrogen atoms are given in Table 4.

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30858 (9 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Fractional coordinates* (× 10^4) *of the heavy atoms*

Estimated standard deviations in units of the last decimal place are given in parentheses.

	x/a	*y/b*	*z/c*
C(1)	3926 (3)	−3847 (3)	2698 (2)
C(2)	4894 (3)	−3590 (3)	1913 (2)
C(3)	4350 (3)	−3230 (3)	832 (2)
C(4)	3518 (3)	−4177 (3)	371 (2)
C(5)	2600 (3)	−4564 (3)	1131 (2)
C(6)	1507 (3)	−4864 (3)	760 (2)
C(7)	635 (3)	−5358 (3)	1449 (2)
C(8)	828 (3)	−5381 (3)	2505 (2)
C(9)	1936 (3)	−4829 (3)	3042 (2)
C(10)	3002 (3)	−4779 (3)	2295 (2)
C(11)	1536 (3)	−3642 (3)	3539 (2)
C(12)	542 (3)	−3832 (3)	4317 (2)
C(13)	−535 (3)	−4479 (3)	3802 (2)
C(14)	−81 (3)	−5654 (3)	3298 (2)
C(15)	−1209 (3)	−6348 (3)	2994 (2)
C(16)	−2031 (3)	−6056 (3)	3911 (2)
C(17)	−1428 (3)	−5032 (3)	4571 (2)
C(18)	−1188 (3)	−3700 (3)	2964 (2)
C(19)	3587 (3)	−6034 (3)	2329 (2)
C(20)	−2347 (3)	−4216 (3)	5063 (2)
C(21)	−1795 (3)	−3171 (3)	5691 (2)
C(22)	−3110 (3)	−4926 (3)	5786 (2)
C(23)	−4271 (3)	−4983 (3)	5691 (2)
C(24)	−5074 (3)	−5628 (3)	6433 (2)
C(25)	−5812 (3)	−4753 (4)	7079 (2)
C(26)	−5019 (4)	−4009 (4)	7836 (3)
C(27)	−6611 (4)	−3945 (4)	6368 (3)
C(28)	−5867 (4)	−6523 (4)	5806 (3)
C(31)	2553 (3)	−464 (3)	496 (2)
C(32)	1752 (3)	−668 (3)	1272 (2)
C(33)	898 (3)	197 (3)	1443 (2)
C(34)	823 (3)	1245 (3)	874 (2)
C(35)	1650 (3)	1415 (3)	123 (2)
C(36)	2519 (3)	597 (3)	−88 (2)
C(37)	3476 (3)	−1378 (3)	226 (2)
O(1)	−861 (2)	605 (3)	2237 (2)
O(2)	3975 (2)	−1357 (3)	−586 (2)
O(3)	3623 (2)	−2161 (2)	1023 (2)
O(4)	205 (2)	−877 (2)	2859 (2)
O(5)	2503 (2)	2863 (2)	−905 (2)
O(6)	621 (2)	3021 (2)	−623 (2)
N(1)	12 (3)	−49 (3)	2236 (2)
N(2)	1599 (3)	2537 (3)	−518 (2)

Accuracy of the refinement

Since the refinement was carried out in block-diagonal approximation to the matrix of normal equations we arbitrarily added 40% to the computed estimated standard deviations (e.s.d.'s) and arrive in this way at respective average e.s.d.'s of 0·0050, 0·0056, 0·0058, 0·0063 and 0·046 Å for the bond lengths N–O, C–O, C–N, C–C and C–H, and average e.s.d.'s of 0·3 and 0·5° for valency and torsion angles not involving hydrogen. Assuming that all observed C(*sp*^{3}–H bond lengths belong to one population one finds an average value of 1·00 Å for this entity with a standard deviation of 0·047 Å, in excellent agreement with the corrected least-squares estimation.

On the other hand the observed deformation of the DNB moiety [see Fig. 1(*d*) and (*e*): *e.g.* the irregular bond lengths in the benzene ring, the difference of 0·022 Å between the bonds C(33)–N(1) and C(35)–N(2) and bond N(2)–O(5) being 0·018 Å shorter than the other three N–O bonds] poses the question as to whether these irregularities are significant, or to put it an other way whether our estimation of standard errors is over-optimistic. If one displaces C(35) by 0·022 Å along the line C(35)–N(2) in such a way that the bonds C(33)–N(1) and C(35)–N(2) become equal, the irregularity of the benzene ring is largely neutralized: bonds C(34)–C(35) and C(35)–C(36) are enlarged to acceptable values of 1·387 and 1·392 Å; valency angles α(33–34–35) α(34–35–36), α(35–36–37), α(34–35–N) and α(36–35–N) are adjusted to more agreeable values of 117·5, 122·0, 118·7, 119·4 and 118·6°, respectively.

The displacement of C(35) can, however, be rejected by means of the *R*-ratio test (Hamilton, 1965). The R'_w value of the model in which the position of C(35)

Table 3. *Thermal parameters* U_{ij}(× 10^3 Å^2) *of the heavy atoms*

Estimated standard deviations in units of the last decimal place are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{21}$	$2U_{23}$	$2U_{31}$
C(1)	17 (2)	18 (2)	16 (2)	3 (3)	6 (3)	7 (2)
C(2)	13 (1)	18 (2)	29 (2)	−2 (3)	0 (3)	9 (3)
C(3)	18 (2)	11 (1)	24 (2)	9 (3)	2 (3)	23 (3)
C(4)	23 (2)	15 (2)	16 (2)	3 (3)	−1 (3)	13 (3)
C(5)	20 (2)	10 (2)	19 (2)	9 (3)	−3 (3)	17 (3)
C(6)	25 (2)	12 (2)	18 (2)	7 (3)	−3 (3)	6 (3)
C(7)	20 (2)	13 (2)	23 (2)	1 (3)	−10 (3)	5 (3)
C(8)	15 (2)	7 (1)	24 (2)	3 (2)	−2 (3)	16 (3)
C(9)	16 (1)	10 (1)	20 (2)	3 (3)	2 (3)	12 (2)
C(10)	16 (1)	9 (1)	22 (2)	7 (3)	3 (3)	12 (2)
C(11)	14 (1)	16 (2)	19 (2)	−1 (3)	−5 (3)	6 (2)
C(12)	16 (2)	13 (2)	22 (2)	−2 (3)	−11 (3)	10 (3)
C(13)	15 (2)	9 (1)	19 (2)	0 (2)	−2 (3)	9 (2)
C(14)	22 (2)	6 (1)	21 (2)	0 (3)	−6 (3)	16 (3)
C(15)	23 (2)	11 (2)	35 (2)	−6 (3)	−13 (3)	22 (3)
C(16)	25 (2)	10 (2)	27 (2)	−6 (3)	−5 (3)	18 (3)
C(17)	17 (1)	11 (2)	15 (1)	2 (3)	5 (3)	6 (2)
C(18)	18 (2)	13 (2)	22 (2)	3 (3)	6 (3)	9 (3)
C(19)	22 (2)	12 (2)	27 (2)	10 (3)	8 (3)	19 (3)
C(20)	17 (2)	12 (1)	14 (1)	3 (3)	1 (3)	10 (2)
C(21)	22 (2)	16 (2)	23 (2)	−3 (3)	−8 (3)	16 (3)
C(22)	23 (2)	12 (2)	17 (2)	8 (3)	1 (3)	7 (3)
C(23)	24 (2)	12 (2)	15 (2)	5 (3)	3 (3)	3 (3)
C(24)	19 (2)	15 (2)	20 (2)	−2 (3)	10 (3)	3 (3)
C(25)	17 (2)	22 (2)	30 (2)	3 (3)	17 (3)	21 (3)
C(26)	42 (2)	29 (2)	37 (2)	−8 (4)	−13 (4)	42 (4)
C(27)	36 (2)	55 (3)	52 (3)	47 (4)	49 (5)	30 (4)
C(28)	43 (2)	25 (2)	34 (2)	−35 (4)	2 (4)	5 (4)
C(31)	19 (2)	13 (2)	18 (2)	0 (3)	−1 (3)	7 (3)
C(32)	20 (2)	9 (1)	18 (2)	−3 (3)	0 (3)	−3 (2)
C(33)	16 (1)	14 (2)	19 (2)	−2 (3)	−8 (3)	6 (2)
C(34)	18 (2)	11 (2)	23 (2)	−1 (3)	−7 (3)	5 (3)
C(35)	23 (2)	9 (2)	19 (2)	−4 (3)	1 (3)	−2 (3)
C(36)	16 (2)	14 (2)	21 (2)	−5 (3)	−2 (3)	8 (3)
C(37)	19 (2)	12 (2)	24 (2)	−3 (3)	4 (3)	8 (3)
O(1)	30 (1)	23 (1)	48 (2)	20 (2)	1 (3)	36 (2)
O(2)	37 (1)	21 (1)	36 (1)	19 (2)	17 (2)	37 (2)
O(3)	21 (1)	13 (1)	23 (1)	8 (2)	3 (2)	16 (2)
O(4)	32 (1)	23 (1)	23 (1)	−1 (2)	7 (2)	18 (2)
O(5)	36 (1)	16 (1)	41 (2)	−2 (2)	13 (2)	24 (2)
O(6)	32 (1)	15 (1)	30 (1)	15 (2)	0 (2)	−3 (2)
N(1)	25 (1)	19 (1)	21 (1)	−4 (3)	−9 (2)	15 (2)
N(2)	29 (2)	11 (1)	24 (1)	1 (2)	−4 (2)	6 (2)

Table 4. *Fractional coordinates* (*in* 10^3 *units*) *and isotropic B values of the hydrogen atoms* (10 Å^2 *units*)

Estimated standard deviations in units of the last decimal are given in parentheses.

	x/a	y/b	z/c	B_{iso}
H(1*A*)	428 (3)	−401 (3)	340 (2)	8 (6)
H(1*B*)	349 (3)	−315 (3)	291 (3)	17 (7)
H(2*A*)	551 (3)	−302 (3)	225 (3)	19 (7)
H(2*B*)	540 (3)	−426 (4)	175 (3)	29 (8)
H(3)	495 (2)	−302 (3)	33 (2)	3 (6)
H(4*A*)	404 (3)	−478 (4)	10 (3)	24 (7)
H(4*B*)	315 (2)	−399 (3)	−32 (2)	4 (5)
H(6)	129 (2)	−482 (3)	4 (2)	3 (5)
H(7)	−7 (2)	−556 (3)	113 (2)	5 (6)
H(9)	221 (2)	−535 (2)	366 (2)	1 (5)
H(11*A*)	219 (2)	−333 (2)	397 (2)	−5 (5)
H(11*B*)	129 (2)	−308 (3)	294 (2)	4 (5)
H(12*A*)	88 (3)	−423 (3)	498 (3)	15 (7)
H(12*B*)	29 (3)	−304 (3)	463 (3)	20 (7)
H(14)	30 (2)	−604 (3)	396 (2)	7 (6)
H(15*A*)	−160 (3)	−610 (3)	221 (3)	18 (7)
H(15*B*)	−107 (4)	−708 (5)	286 (3)	48 (11)
H(16*A*)	−280 (2)	−583 (3)	357 (2)	2 (5)
H(16*B*)	−221 (3)	−670 (3)	439 (2)	12 (6)
H(17)	−95 (2)	−530 (2)	520 (2)	0 (5)
H(18*A*)	−75 (3)	−349 (4)	235 (3)	22 (9)
H(18*B*)	−153 (3)	−292 (3)	330 (2)	18 (7)
H(18*C*)	−199 (3)	−395 (3)	262 (3)	18 (7)
H(19*A*)	290 (3)	−661 (3)	209 (3)	22 (7)
H(19*B*)	420 (3)	−613 (3)	184 (2)	11 (6)
H(19*C*)	398 (3)	−617 (3)	308 (2)	13 (7)
H(20)	−288 (2)	−394 (3)	441 (2)	8 (6)
H(21*A*)	−115 (3)	−334 (3)	623 (3)	16 (7)
H(21*B*)	−142 (3)	−266 (3)	518 (2)	11 (6)
H(21*C*)	−238 (3)	−271 (3)	608 (2)	12 (6)
H(22)	−270 (3)	−529 (4)	641 (3)	24 (8)
H(23)	−463 (2)	−464 (3)	512 (2)	3 (5)
H(24)	−457 (2)	−600 (3)	696 (2)	6 (5)
H(25)	−642 (3)	−522 (4)	757 (3)	26 (8)
H(26*A*)	−459 (4)	−456 (5)	844 (4)	68 (14)
H(26*B*)	−555 (3)	−346 (3)	825 (2)	11 (6)
H(26*C*)	−444 (3)	−359 (4)	748 (3)	32 (9)
H(27*A*)	−607 (4)	−342 (4)	587 (4)	48 (11)
H(27*B*)	−718 (4)	−432 (4)	583 (3)	51 (11)
H(27*C*)	−705 (4)	−340 (4)	693 (4)	52 (11)
H(28*A*)	−639 (3)	−697 (4)	634 (3)	40 (9)
H(28*B*)	−641 (3)	−619 (3)	519 (3)	20 (7)
H(28*C*)	−540 (3)	−714 (4)	545 (3)	36 (9)
H(32)	174 (2)	−133 (3)	174 (2)	6 (6)
H(34)	17 (3)	169 (3)	98 (3)	18 (7)
H(36)	307 (2)	73 (3)	−66 (2)	3 (5)

is fixed amounts to 4·86%, hence the ratio R'_w/R_w is 1·008. Consider the function $R(v, N, \alpha)$ where v is the number of fixed parameters (3), N the number of degrees of freedom [the number of significant reflexions (3864) minus the number of parameters (551)] and α is the significance level of the test. Since the function $R(3, 3313, 0{\cdot}005)$ has the value 1·002, there is one chance in more than 200 that the constrained model is falsely rejected.

Molecular geometry

Bond lengths, valency and endocyclic torsion angles are given in Fig. 1. The overall geometry is depicted in Fig. 2. Some salient Newman projections are shown in Fig. 3, while geometric entities not given in Figs. 1 and 3 are listed in Table 5.

(i) *The steroid nucleus*

The mean value of C(sp^3–C(sp^3) bond lengths [1·541 (1) Å] is rather high in comparison with the commonly observed value of 1·533 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). The corresponding mean values for lumisterol$_3$ (de Kok & Romers, 1974), isopyrocalciferol (de Kok, Hogendorp & Romers, to be published),

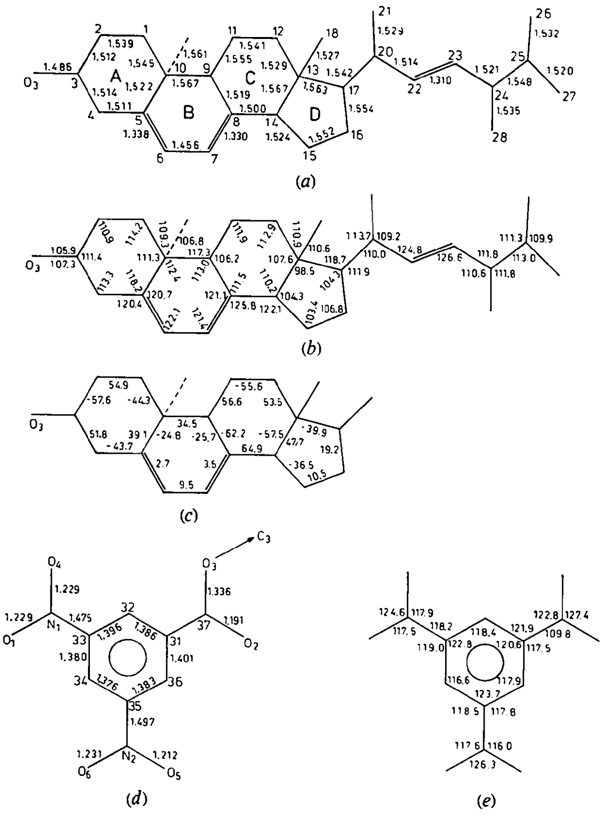

Fig. 1. (*a*) Bond distances (Å) and numbering of atoms of the PCD moiety. (*b*) Valency angles (°). [α (1–10–9) = 110·9, α (5–10–19) = 105·8, α)12–13–17) = 117·1, α (14–13–18) = 111·4, α (3–O_3–37) = 117·5°.] (*c*) Torsion angles (°). (*d*) Bond distances and numbering of the DNB moiety. (*e*) Valency angles of the DNB moiety.

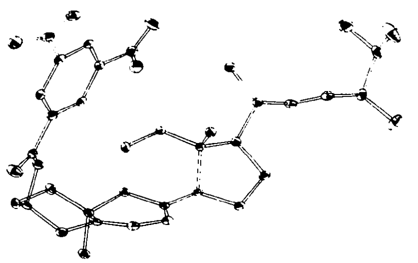

Fig. 2. An *ORTEP* projection of the molecule (Johnson, 1967).

5α,17α-pregnane-3β,20α-diol (Romers, de Graaff, Hoogenboom & Rutten, 1974), 3α,3β-dimethoxy-5α-oestran-17β-toluene-*p*-sulphonate (de Graaff, van der Ende & Romers, 1974) and 3-oxo-5α-androstan-17β-toluene-*p*-sulphonate (de Graaff & Romers, 1974) are 1·536 (1), 1·536 (3), 1·531 (1), 1·530 (2) and 1·534(2) Å, respectively. The relatively large mean value for PCD might indicate that a larger part of the strain is absorbed in the distances than normally.

Inspection of Fig. 1(*a*) shows that bonds C(9)–C(10), C(15)–C(16), C(16)–C(17) and C(13)–C(17) are rather long, a common feature of most steroid molecules (Romers, Altona, Jacobs & de Graaff, 1974). The bond lengths C(9)–C(11) (1·555 Å) and C(10)–C(19) (1·561 Å) also deviate significantly from the standard value of 1·533 Å. On the other hand the bonds C(2)–C(3) and C(3)–C(4), neighbours of the ester linkage C(3)–O(3), are rather short, a well known feature of steroids with a hydroxy group or an ester linkage at C(3).

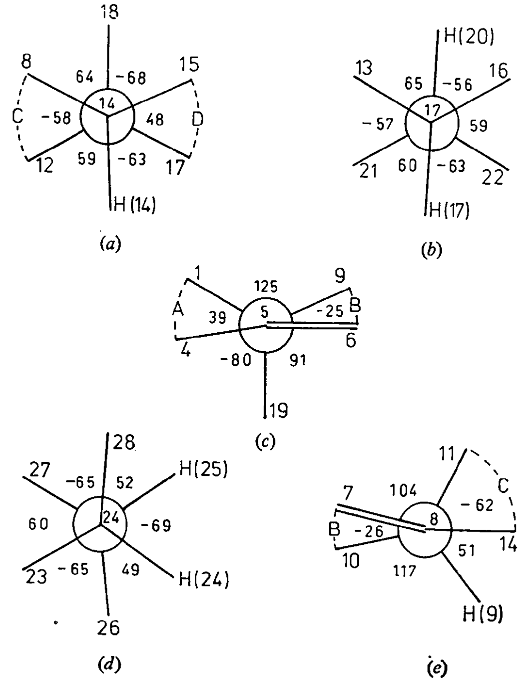

Fig. 3. Newman projections along (*a*) 14–13, (*b*) 17–20, (*c*) 8–9, (*d*) 5–10 and (*e*) 24–25.

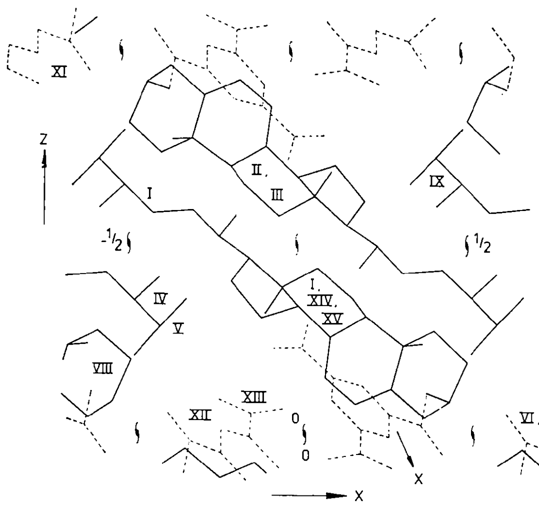

Fig. 4. A projection of the structure along [010]. The dashed lines refer to the DNB moiety.

Table 5. *Molecular entities of PCD not indicated in Fig.* 1

Distances are in Å, angles in decimal degrees. Numbers in parentheses are e.s.d.'s in units of the last decimal place.

Mean distances

C(sp^3)–C(sp^3)	1·5408 (14)	Single
C(sp^3)–C(sp^2)	1·514 (2)	Single
C(sp^2)–C(sp^2)	1·456 (6)	Single
C(sp^2)=C(sp^2)	1·326 (3)	Double
C(sp^2)–C(sp^2)	1·387 (2)	Aromatic
C(sp^3)–H	1·00 (1)	Saturated
C(sp^2)–H	0·93 (2)	Otherwise

Mean bond angles

C——C(sp^3)–C	111·86 (5)	Saturated with exclusion of ring *D* and quaternary carbon atoms
H——C(sp^3)–C	111·8 (2)	No specification
H——C(sp^3)–H	105·0 (4)	No specification

Least-squares plane of the benzene ring with reference to orthogonal axes **a**, **b** and **c***

$$-0{\cdot}5826X-0{\cdot}4301Y-0{\cdot}6896Z+1{\cdot}8691=0$$

Deviations from the least-squares plane

C(31)	0·008	C(36)	−0·004	O(2)	0·395
C(32)	−0·004	C(37)	0·066	O(3)	−0·306
C(33)	−0·003	N(1)	0·047	O(4)	−0·190
C(34)	0·006	N(2)	0·014	O(5)	−0·421
C(35)	−0·003	O(1)	0·304	O(6)	0·508

Contrary to the frequently observed rule (Geise, Altona & Romers, 1967) that the 'inner' valency angles about the quarternary carbon atom C(10) are smaller than 109·5°, we observe for PCD [*cf.* Fig. 1(*b*)] that these angles are significantly larger than 109·5°. Their sum amounts to 223·7 (2)°, in striking contrast to the standard value of 214·9 (1)° observed for 17 steroids with normal 5α-configuration (Romers, Altona, Jacobs & de Graaff,), 1974).

Ring *A* displays the same characteristics as ring *A* of lumisterol$_3$. It is a distorted slightly flattened chair. It has approximate C_2 symmetry with the dyad running through the midpoints of the bonds C(2)–C(3) and C(5)–C(10). Ring *B*, with a 1–3 diplanar conformation, also closely resembles the corresponding ring of lumisterol. It displays C_2 symmetry with the dyad running through the midpoints of the bonds C(6)–C(7) and C(9)–C(10). The equal and positive signs of the torsion angles φ(5–6–7–8) are in agreement with the prediction derived from the observed Cotton effect (Jacobs, 1972).

Ring *C* has a normal slightly distorted chair conformation with a rather heavy puckering. Only φ(11–12–13–14) is distinctly smaller than the standard value of cyclohexane (55·9°; Geise, Buys & Mijlhoff, 1971). Its symmetry is approximately reduced to the point group C_s with a mirror plane through C(8) and C(12). Ring *D* is characterized by the maximum puckering angle $\varphi_m = 47{\cdot}5°$ and phase angle $\Delta = 15{\cdot}5°$ (Altona, Geise & Romers, 1968). Its conformation is $C_2(16)$–$C_s(13)$, *i.e.* intermediate between a half-chair and an envelope.

Inspection of Fig. 3(*a*) and (*b*) indicates the nearly antiplanar configuration of H(14) and C(18) and of H(17) and H(20), the dihedral angles φ[H(14)–14–13–18] and φ[H(17)–17–20–H(20)] having values of 179 and 178°, respectively. The torsion angles about the joint 8–9 connecting rings *B* and *C* [Fig. 3(*e*)] have equal signs. This type of ring junction (Jacobs, 1972) is rather unusual and occurs provided φ(7–8–9–10) is rather small and φ(14–8–9–11) attains a fairly large value.

In Table 6 are listed the geometric entities of the steroid nucleus of PCD together with the corresponding 'theoretical' values (Romers *et al.*, 1974) obtained by means of a valence force-field calculation (Faber & Altona, 1974) of 9α,10α-androsta-5,7-dien-3β-. With the exception of bonds 13–14, 13–17 and 13–18, and external bond angles 10–9–11, 14–8–9 and 15–14–8 the agreement is rather good. As can be expected, the agreement is less satisfactory for the torsion angles. Nonetheless the shapes of the rings and all signs of torsion angles are reproduced correctly.

(ii) *The 17β side chain*

Inspection of Fig. 2 indicates that the side chain of PCD is not stressed. Comparison of the dihedral angles (Table 7) of the sidechains of lumisterol$_3$, pyro- and isopyrocalciferol reveals that the cholestane side-chain of the first compound is stressed while the ergostane side chains are folded in an almost identical manner. This is in agreement with the earlier observation (Romers *et al.*, 1974) that the cholestane side chains are fully stressed, while the ergostane side chains display bends about the bonds 20–22 and 23–24. According to the Cahn, Ingold & Prelog rules (1966) the chain has *R* chirality at C(20) and C(24).

(iii) *The* 3,5-*dinitrobenzoate ester moiety*

As shown above the benzene ring is slightly distorted. The distortion does not, however, involve a deviation from planarity: the maximum deviation from the least-squares plane through the benzene carbon atoms [0·0079 Å for C(31)] being insignificant in view of the attained accuracy. On the other hand the nitro and carboxyl groups (Table 5) deviate from the least-squares plane to the extent that the groups are tilted and simultaneously bent out of the plane of the benzene ring. The bends of N(1), N(2) and C(37) are small (~0·04 Å) and in the same direction. The tilts of the groups O(2)–C(37)–O(3), O(1)–N(1)–O(4) and O(5)–N(2)–O(6) are not in the same direction and amount to 17, −13 and 25°, respectively.

Table 6. *Experimental and calculated geometrical entities of PCD*

The calculated values (Romers, Altona, Jacobs & de Graaff, 1974) are derived from 9α,10α-androsta-5,7-diene-3-ol.

Bond distances (Å)			Bond angles (°)			Torsion angles (°)		
	Exp.	Calc.		Exp.	Calc.		Exp.	Calc.
1–2	1·539	1·531	10—1—2	114·2	114·9	*A*		
1–10	1·545	1·534	1—2—3	110·9	109·6	1–10	−44·3	−49·7
2—3	1·512	1·528	2—3—4	111·4	110·0	1—2	54·9	58·4
3—4	1·514	1·522	3—4—5	113·3	113·4	2—3	−57·6	−57·5
4—5	1·511	1·515	4—5-10	118·2	117·0	3—4	51·8	52·9
5-10	1·522	1·524	5-10—1	111·3	109·2	4—5	−43·7	−47·6
5—6	1·338	1·343	4—5—6	120·4	120·8	5-10	39·1	43·9
6—7	1·456	1·449	1-10—9	110·9	109·8	*B*		
7—8	1·330	1·341	1-10-19	109·3	110·6	5-10	−24·8	−31·5
8—9	1·519	1·515	9-10-19	106·8	109·0	5—6	2·7	3·3
9-10	1·567	1·570	9-10—5	112·4	110·5	6—7	9·5	12·9
9-11	1·555	1·547	10—5—6	120·7	120·1	7—8	3·5	3·4
11-12	1·541	1·550	5—6—7	122·1	121·5	8—9	−25·7	−31·9
12-13	1·529	1·530	6—7—8	121·4	121·3	9-10	34·5	43·8
13-14	1·567	1·522	7—8—9	121·1	120·0	*C*		
8-14	1·500	1·505	8—9-10	113·0	111·4	8—9	−62·2	−57·6
14-15	1·524	1·535	7—8-14	125·8	123·0	9-11	56·6	50·9
15-16	1·552	1·549	10—9-11	117·3	122·7	11-12	−55·6	−51·8
16-17	1·554	1·548	8-14-13	110·2	110·2	12-13	53·5	52·8
13-17	1·563	1·532	14—8—9	111·5	114·6	13-14	−57·5	−55·7
13-18	1·529	1·545	8—9-11	106·2	107·7	8-14	64·9	61·5
10-19	1·561	1·550	9-11-12	111·9	112·2			
			11-12-13	112·9	114·0			
			12-13-14	107·6	109·2			
			15-14—8	122·1	126·3			
			12-13-17	117·1	115·7			
			12-13-18	110·9	109·7			
			14-13-18	111·4	111·5			

Table 7. *Dihedral angles (decimal degrees) in the side-chain of lumisterol$_3$, pyro- and isopyrocalciferol*

Dihedral angle	Pyro-calciferol	Isopyro-calciferol	Lumisterol
φ(13–17–20–21)	−56·7	−54·0	−54
φ(13–17–20–22)	−179·5	−176·0	−178
φ(17–20–22–23)	−124·0	−103·7	−179
φ(20–22–23–24)	−176·4	−173·3	−176
φ(22–23–24–25)	110·7	133·5	176
φ(23–24–25–26)	−64·8	−54·9	72
φ(23–24–25–27)	59·5	70·4	195

Irregular benzene rings are quite often observed in phenyl and benzyl fragments. Table 8 presents the bond lengths of 13 benzene rings occurring in 11 compounds published recently. Only three rings have a maximum deviation from the mean value which is smaller than 0·008 Å.

(iv) *The overall shape of the molecule*

Fig. 2. shows that the molecule is 'L' or rather 'V' shaped. This remarkable form is achieved by the combined action of (1) the axial bond C(3)–O(3) with respect to ring *A*; (2) the deviation (5°) from collinearity of the bonds C(3)–O(3) and C(37)–C(31); (3) the twist (17°) of the benzene nucleus with respect to the plane of C(3), O(3), O(2) and C(37) in such a way that the nitro group O(1)–N(1)–O(4) fills up the empty space between the benzene ring and steroid ring *C*; (4) the fold of ring *C* with respect to the roughly parallel orientation of rings *A* and *B*.

The fold of ring *C* is a direct consequence of the 9α, 10α configuration which forces C(11) to an upward position (Fig. 2).

Packing

Part of the crystal structure is illustrated in Fig. 4 in a projection along [010]. The DNB moiety is indicated by dashed lines. The PCD part roughly parallels the direction [$\bar{3}$02]. Intermolecular interactions of the type H···H and O···H within 3·0 Å are presented in

Table 9. *Intermolecular interactions within* 3·0 Å

The reference molecule is i at x,y,z. Distances are in Å.

Molecule	Operation			Number of interactions	Average distance	Minimum distance
(*a*) H···H interactions						
ii	$-x$	$-\frac{1}{2}+y$	$1-z$	16	2·74	2·30
iii	$-x$	$\frac{1}{2}+y$	$1-z$	16	2·74	2·30
iv	$-1-x$	$-\frac{1}{2}+y$	$1-z$	11	2·76	2·54
v	$-1-x$	$\frac{1}{2}+y$	$1-z$	11	2·76	2·54
vi	$1-x$	$-\frac{1}{2}+y$	$-z$	3	2·63	2·25
vii	$1-x$	$\frac{1}{2}+y$	$-z$	3	2·63	2·25
viii	$-1+x$	y	z	6	2·68	2·38
ix	$1+x$	y	z	6	2·68	2·38
x	$1+x$	y	$-1+z$	4	2·67	2·45
xi	$-1+x$	y	$1+z$	4	2·67	2·45
xii	$-x$	$\frac{1}{2}+y$	$-z$	2	2·67	2·64
xiii	$-x$	$-\frac{1}{2}+y$	$-z$	2	2·67	2·64
(*b*) O···H interactions						
ii	$-x$	$-\frac{1}{2}+y$	$1-z$	3	2·87	2·62
iii	$-x$	$\frac{1}{2}+y$	$1-z$	3	2·87	2·62
iv	$-1-x$	$-\frac{1}{2}+y$	$1-z$	1	2·99	2·99
v	$-1-x$	$\frac{1}{2}+y$	$1-z$	1	2·99	2·99
vi	$1-x$	$-\frac{1}{2}+y$	$-z$	3	2·82	2·67
vii	$1-x$	$\frac{1}{2}+y$	$-z$	3	2·82	2·67
xii	$-x$	$\frac{1}{2}+y$	$-z$	2	2·83	2·77
xiii	$-x$	$-\frac{1}{2}+y$	$-z$	2	2·83	2·77
x	$1+x$	y	$-1+z$	1	2·85	2·85
xi	$-1+x$	y	$1+z$	1	2·85	2·85
xiv	x	$1+y$	z	3	2·76	2·67
xv	x	$-1+y$	z	3	2·76	2·67

Table 10. *Interactions involving the nitro groups*

Distances are in Å.

(*a*) Intramolecular			
O(4)···H(18*B*)	3·09	O(4)···H(11*B*)	2·77
(*b*) Intermolecular			
O(1)···H(6)	2·90	N(1)···O(6)	3·03
O(1)···H(15*B*)	2·75	O(6)···H(18*A*)	2·77
O(1)···H(27*B*)	2·86	O(6)···H(6)	2·67
O(4)···H(17)	2·62	O(6)···H(7)	2·86
O(4)···H(22)	2·99	O(6)···O(4)	3·16
O(4)···O(6)	3·16	O(6)···N(1)	3·03

Table 8. *Carbon–carbon bond lengths of some benzene rings, mean lengths* $\langle r \rangle$, *e.s.d.* $\sigma(r)$ *and maximum deviation from the mean value* δ *in* Å

Reference*	1–2	2–3	3–4	4–5	5–6	1–6	$\langle r \rangle$	$\sigma(r)$	δ
(1)	1·401	1·383	1·376	1·380	1·396	1·384	1·387	0·006	0·014
(2)	1·383	1·382	1·380	1·366	1·378	1·385	1·380	0·006	0·014
(3)	1·388	1·370	1·393	1·402	1·410	1·359	1·387	0·007	0·017
(4)	1·400	1·377	1·387	1·401	1·388	1·388	1·390	0·009	0·013
(5)	1·394	1·396	1·371	1·379	1·393	1·393	1·388	0·003	0·017
(6)	1·404	1·384	1·389	1·389	1·384	1·404	1·392	0·004	0·012
(7)	1·402	1·390	1·383	1·376	1·395	1·393	1·390	0·005	0·014
(8)	1·388	1·380	1·385	1·386	1·393	1·387	1·386	0·007	0·007
(9)	1·393	1·391	1·385	1·389	1·396	1·388	1·390	0·003	0·006
(10)	1·407	1·381	1·357	1·397	1·391	1·392	1·388	0·007	0·031
(10)	1·393	1·368	1·371	1·374	1·387	1·376	1·378	0·006	0·015
(11)	1·400	1·387	1·387	1·392	1·393	1·406	1·394	0·002	0·006
(11)	1·403	1·392	1·394	1·396	1·392	1·406	1·397	0·002	0·009

* (1) This work. (2) Isopyrocalciferol, to be published. (3) de Graaff & Romers (1974). (4) de Graaff, van der Ende & Romers (1974). (5) Shaw & Fratini (1974). (6) Zettler, Hausen & Hess (1974). (7) Chiaroni, Riche & Pascard-Billy (1974). (8) Cameron, Freer, Doyle & Wright (1974). (9) van der Ende, Offereins & Romers (1974). (10) Dreissig, Luger & Rewicki (1974). (11) Hoekstra.

Table 9. The molecules are tightly packed and surrounded by 14 neighbouring molecules.

Adopting van der Waals radii of 1·2, 1·5 and 1·7 Å for hydrogen, nitrogen and carbon and of $1{\cdot}5_5$ Å for the partly negatively charged oxygen of the nitro groups one finds (Table 10) nine interactions, including two intramolecular interactions between the nitro group O(1)–N(1)–O(4) and neighbouring atoms having distances equal to about the sum of the van der Waals radii. The O(5)–N(2)–O(6) group only displays five such intermolecular and no intramolecular interactions. The relatively loose packing of the latter nitro group might explain, at least partly, why the distance N(2)–C(35) is larger than its counterpart N(1)–C(32).

The calculations were performed on IBM 360/65 and 370/158 computers of the University of Leiden.

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